ACTIVITY REPORT

December 2001

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

Los Alamos
Los Alamos, NM 87545
(505) 667-7811

Sandia
Albuquerque, NM 87185
(505) 844-7333

Lawrence Livermore
Livermore, CA 94551
(925) 422-5196

Lawrence Berkeley
Berkeley, CA 94720
(510) 486-5085

Argonne
Argonne, IL 60439
(202) 488-2415

Brookhaven
Upton, NY 11973
(516) 344-3819

Idaho
Idaho Falls, ID 83415
(208) 526-7004

Oak Ridge
Oak Ridge, TN 37831
(865) 574-4977

Pacific Northwest
Richland, WA 99352
(509) 376-4565

To: William F. Lawson, Director
National Petroleum Technology Office
U.S. Department of Energy
P.O. Box 3628
Tulsa, OK 74101

From: J. Albright, Los Alamos
D.J. Borns, Sandia
J. Ziagos, Lawrence Livermore
G.M. Hoversten, Lawrence Berkeley
D. Schmalzer, Argonne
A. Goland, Brookhaven
C. Thomas, Idaho
T. Schmidt, Oak Ridge
B. Saffell, Pacific Northwest

cy: G. Dehoratiis, DOE Fossil Energy
E. Allison, DOE Fossil Energy
L. Capitanio, DOE Fossil Energy
A. Hartstein, DOE Fossil Energy
B. Hochheiser, DOE Fossil Energy
E. Subia-Melchert, DOE Fossil Energy
N.B. Woodward, DOE Office of Science
D. Alleman, DOE-NPTO-Tulsa
J. Casteel, DOE-NPTO-Tulsa
N. Comstock, DOE-NPTO-Tulsa
B. Lemmon, DOE-NPTO-Tulsa
R. Lindsey, DOE-NPTO-Tulsa
R. Long, DOE-NPTO-Tulsa
K. Sterling, DOE-NPTO-Tulsa
D. Sutterfield, DOE-NPTO-Tulsa
J. Ammer, NETL
F. Brown, NETL
H. Guthrie, NETL
B. Gwilliam, NETL
J. Rogers, NETL
B. Tomer, NETL
F. Toro, NETL
A. Yost, NETL

Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Oil and Gas Recovery Technology	Upstream Environmental Technology
Drilling, Completion, and Stimulation Technology	Downstream Environmental Technology
Diagnostic and Imaging Technology	Ultra-Clean Fuels Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources

(ChevronTexaco and SNL)

Report not received.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water

(Baker Hughes, ChevronTexaco, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Unocal, and ORNL)

Report not received.

Reducing Chemical Use and Toxicity in Produced-Water Systems

(BP Amoco, Rhorback Casasco Systems, and ANL)

Highlights:

- Transfer of ECN corrosion probe technology at a refinery initiated.
- U.S. patent for a new electrode design for monitoring pitting corrosion issued.
- Presentation given at the 8th Annual International Petroleum Environmental Conference.

The purposes of this project are 1) to minimize the environmental discharge of hydrocarbons and treatment chemicals due to failures resulting from sustained localized pitting corrosion, 2) to reduce the use of toxic treatment chemicals used by field operators to prevent those failures, and 3) to identify treatment approaches that reduce the use of toxic chemicals. The approach in this project is to develop an on-line, real-time method to monitor sustained localized pitting so that treatment chemicals (e.g. biocides and chemical inhibitors) can be applied only when needed.

ANL was granted a U.S. patent for a new electrode design for corrosion monitoring. This patent describes an electrode that increases the sensitivity of the electrochemical noise (ECN) probe for monitoring the development of sustained localized pitting corrosion. A publication, "Monitoring and mitigation of sustained, localized pitting corrosion," was published in the proceedings of the 8th International Petroleum and Environmental Conference, Houston, TX.

Efforts continue to transfer ANL's ECN technology to industry participants. A November meeting was held in Texas with Equilon Enterprises, LLC, to discuss a collaboration and potential field test of the ECN probe in a refinery. Ondeo (formerly Nalco), a chemical manufacturing and service company, is interested in incorporating ANL's ECN technology into their corrosion and fouling monitoring service that they provide for their clients. Discussion included using the ECN probe to monitor the corrosion on overhead condensers and separation drums in the Equilon facility in Westhollow, TX, or the Mobile, LA, refinery facility. Future meetings are planned to discuss the proposed collaboration between Ondeo, Equilon, and ANL.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- Volumetric productivity deficiencies and limitations in reactor designs and immobilization strategies documented.
- Viable field site identified.
- Presentation given at the 8th Annual International Petroleum Environmental Conference.

Project researchers have documented volumetric productivity deficiencies and limitations in accepted reactor designs and immobilization strategies currently applied in a variety of industrial sectors. Both batch and continuous-stirred bioreactors inoculated with immobilized *thiobacilli* or *thiomicrospira* resulted in rates of sulfide removal that were determined to be noncommercial when sparged with increasing amounts of hydrogen sulfide (H_2S) (g). This was determined to be the result of low density of biocatalysts retained within the porous BioSep beads (estimated 35% biomass inside beads and 65% outside beads) used for the immobilization. To avoid increasing the size of the reactor and associated costs, efforts were undertaken to develop new beads that could better retain/immobilize biomass and improve volumetric productivity. These newer beads, designed for better retention of sulfides and biocatalysts, are currently being evaluated in stirred tank reactors.

Data was collected which suggests that packed bed bioreactors, using biocatalysts immobilized in BioSep beads, may offer increased volumetric productivity vs. fluidized bed reactors.

The best field test site identified thus far is a natural gas field with a well producing 1.4 MMscf/d containing about 3000 ppm H_2S. The operator has determined that the gas is uneconomical to sweeten using conventional technology.

G.E. Jenneman presented "Evaluation of an immobilized *thiomicrospira* sp. strain CVO enrichment for H_2S oxidation," which was written by G.E. Jenneman, K. Sublette, S. Harmon, G A Bala, and T. Ward, at the 8th Annual International Petroleum Environmental Conference, Albuquerque, NM.

It was anticipated that the project would be taken to the field in FY01. However, the research findings (specifically volumetric productivity and catalyst immobilization issues) did not support the anticipated design for implementation. Placement of technology in the field during FY01 would have resulted in a technical success with questionable economic practicality, and greatly reduced commercial scale viability. Therefore, with the support of the National Technology Program Office, the field trial was delayed. This delay allowed the project team to seek additional industry collaborators and make substantial progress towards securing additional collaborative funding to better implement the field trial and transfer the resulting technology, thereby creating a greater benefit to the NGOTP and the DOE.

Characterization of Soluble Organics in Petroleum Waste Water

(ChevronTexaco, Marathon, Phillips, Shell, Statoil, and ORNL)

Report not received.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, Exxon, Gas Technology Institute, Unocal, LBNL, ORNL, and LLNL)

Highlights:

- Development of owl-vole spatial template model begun.
- Preliminary landscape module completed.
- Vegetation biomass and growth module completed.

The intensive modeling phase of the project has begun. The Geographic Information System (GIS) development for the Tall Grass Prairie Preserve (TPP) is essentially complete. Data layers on vegetation type, well location, and representative spill locations are available for use as input into the modeling effort. Site statistics were developed and will be used in the modeling effort.

A web-based user interface for the GIS is complete and accessible to LLNL researchers. Due to heightened computer security concerns, the web site is cur-

rently not accessible to non-LLNL researchers and participants, although researchers are working to change this.

Researchers are creating a simulation model to evaluate the effect of size and distribution of spills and habitat patches on ecological populations at the TPP. The goal is to develop a generic model, or template, that can be used to determine the frequency, size, and distribution of spills leading to a density of herbivores and/or predators that can't persist. Researchers also plan to use the model to quantify how the effects of petroleum-related habitat loss differs for species with different life history attributes, mobility, and spatial habitat requirements.

Researchers started building the first template model using the prairie vole - short-eared owl system. This system was selected because the vole is territorial and has high site and mate fidelity. High site fidelity includes storage of food and long-term burrow occupancy. The vole also comprises the majority of the short-eared owl's diet. The model is a spatially-explicit individual-based model (IBM) with an object-oriented programming structure using the C++ programming language. This type of model was selected because it lends itself best to representing realistic ecological interactions between animals and petroleum activities. Additionally, it facilitates simulation of animal movements that bring populations in contact with human activities. The structure of the template model consists of an hierarchical set of classes, with each class containing a number of objects. Within the ecosystem class, which keeps track of the initial conditions and climatic variables, is a species class and a landscape class. The landscape class contains a basic landscape disturbance grid upon which the species class will interact. Simulations occur on the background of a dynamic landscape that includes prescribed burning and grazing.

Researchers completed a preliminary landscape module that simulates transitions between the landscape states (i.e. burned or grazed). In addition, a preliminary model that predicts vegetation growth and final biomass based on evapo-transpiration was completed.

Finally, a time-zero (initial condition) vegetation grid for use in the initial parameterization of the vole-owl model using the vegetation layer from the GIS was developed. Coding of the vole module is under way.

Estimation and Reduction of Air Quality Modeling Uncertainties (Envair, EPRI, and LBNL)

Highlights:

- Follow-up interviews conducted.
- EPA Associate Director of Health visited LBNL.

Follow-up interviews were conducted for the Central Valley case study using questions developed during transcription and coding of past interviews.

The list of coding categories and category attributes was finalized. The attributes to identify and describe dominant narratives about the uses and uncertainties of modeling systems applied for air quality planning were dimensionalized.

Project researchers continue to transcribe and code interviews using Nvivo software.

A pre-draft of a review paper titled "Treatment of scientific uncertainty in urban air quality regulation" was completed.

The Environmental Protection Agency (EPA) Associate Director of Health visited LBNL for three days in December 2001. LBNL staff briefed him on the Air Quality Model Uncertainty research to inform the EPA of the project.

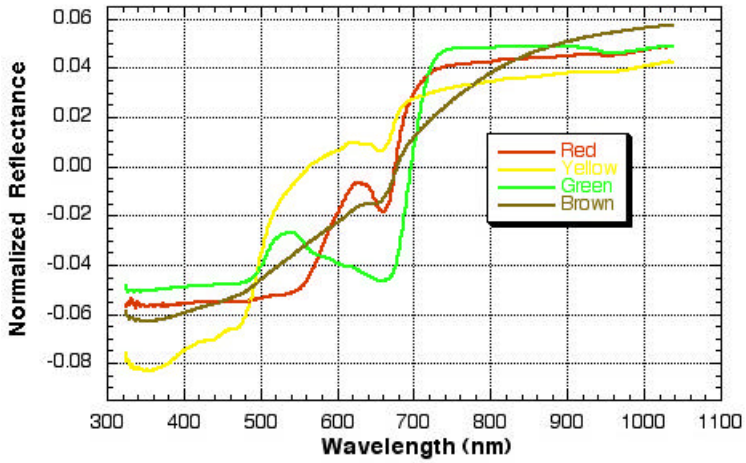
Remote Sensing for Environmental Baselining and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

Highlights:

- Created spectral library.
- Completed geo-referencing for the AVIRIS data from June 2000.

The presence of chlorophyll in green vegetation results in a characteristic red-edge signature, which is strong absorption in the red band followed by strong reflectance in the near infrared (green curve on figure). At the Jornada Experimental Range (JER) near Las Cruces, NM, woody stems, dead plants, and oil-sprayed soil have a characteristic brown spectrum, with reflectance increasing steadily from 400-1050 nm (brown curve in figure). This brown spectrum lacks the red-edge signature. Under stress (the color change in leaves that occurs in autumn is a familiar example), the spectra of green leaves changes; more reflectance in the red causes the leaves to appear yellow, orange, or red and less reflectance in the near infrared decreases the red-edge signature (red and yellow curves in figure).



ORNL developed a spectral library of characteristic spectra for green vegetation, brown vegetation (woody stems and dead plants), soil, and stressed green vegetation. This library has two spectral ranges: Limited (350-1050 nm) and Full (350-2500 nm). The spectra in the library can be used to classify field or remote measurements, to “un-mix” composite spectra, and to detect stress. The library is developed by clustering a collection of field or laboratory measurements and calculating the mean spectrum for each major cluster. The clustering is based on high correlation coefficients; the mean spectra are calculated using singular value decomposition. The spectra were measured at ORNL and the Army Corps of Engineers Topographic Engineering Center (TEC). Spectra in the library include green and brown from the ORNL limited-range measurements at Jornada, and full-range green, brown, and soil from TEC measurements. To create a library of stressed vegetation, ORNL scientists gathered leaves during autumn color and measured their spectra. The limited-range spectra in the library include red, yellow, green, brown, and water (see figure).

On June 1, 2000, a road grader cut an oil pipeline at the JER, causing oil to spray over a five-acre area. The Airborne Visible Infrared Imaging Spectrometer (AVIRIS) hyperspectral sensor was used to collect data at the JER on June 10, just nine days after the oil spray accident. The AVIRIS flights collected data on four north-south paths over the JER. ORNL completed the geo-referencing for the two paths nearest to the spill site (Route 3, to the west and Route 4, to the east). The AVIRIS data image is a strip that is 614 pixels wide and more than 4000 pixels long. Each pixel has 224 bands of reflectance data from a

square region with 17.4-m sides. Geo-referencing was accomplished by measuring the position of features on both the image and on a corresponding topographical map. The measured data were validated by estimating a linear relationship between pixel coordinates, latitude, and longitude (measured in degrees). Unfortunately, the five-acre sprayed area is in the gap between the two paths: the Route 3 image is 1786-m west of the spray site, and the Route 4 image is 236-m east of the spray site. Since the oil ran down a dirt road located within the Route 4 image, the pixels of the Route 4 image that are crossed by the road should have an oil signature.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts

(ChevronTexaco, UOP, and INEEL)

Highlight:

- Final report in preparation.

The project is nearly complete except for one set of experiments that will be performed in January 2001. The final report is in preparation.

The final reaction set will complete the study of the oxidation of dibenzothiophene (DBT) using soybean peroxidase (SBP) in a Supercritical (SC) carbon dioxide (CO_2) emulsions with the perfluoropolyetherammonium carboxylate (PFPE) surfactant. Prior work demonstrated a 4.1% conversion of DBT to product in the SC CO_2 emulsions. Due to the significantly higher solubility of DBT in the Supercritical Fluid (SCF) emulsion, this conversion represented a 17-fold increase in product yield over aqueous phase biocatalysis.

Biological Upgrading of Heavy Oils for Viscosity Reduction

(BP Amoco, ChevronTexaco, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

Report not received.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, ChevronTexaco, Shell, and BNL)

The analysis of crude oils is not a simple task because of its complexity as a mixture of hydrocarbons and hetero-compounds. The analysis of heavy crudes is further complicated by the large fraction of high molecular weight compounds. No single analysis can adequately reveal the reactions that occur. Biochemical upgrading reactions on heavy crude oil is no exception, and it should be evaluated by different analytic methods.

Table 1: Viscosity of dehydrated oil samples

	Untreated Crude Sample	Control Crude Sample	Treated Crude Sample
Viscosity in Centipoises at 30°C	4000	3000	1750

A low-sulfur heavy crude oil (°API = 19.4) was treated with a thermophilic bacterium at 60°C for three days. The control sample was treated in the same way, without the inoculation of bacterium. Both samples were separated from the aqueous layer by centrifugation. A Brookfield viscometer measured the vis-

cosity of the dehydrated samples. The results shown in Table 1 indicate that the viscosity of the control sample was lower than that of the untreated sample. The viscosity of the treated sample was even lower than that of the control sample. The bacteria converted the heavy oil into lighter oil.

Gas chromatograph- mass spectrometry analysis of these samples indicates the treated sample and control sample contain lighter fractions as diesel and fuel oil cuts than the untreated sample. The results support the formal explanation.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(ChevronTexaco, Phillips, ORNL, and INEEL)

Highlight:

- Experiments initiated to improve LiP expression in *Pichia pastoris*.

The objective is to develop new technologies for upgrading heavy oils using novel enzyme-based bioprocessing concepts. Enzymes, naturally active in aqueous environments, will be modified by genetic engineering or chemical modification to make them stable and active in organic media.

Two different experiments were initiated to investigate strategies to improve expression of the lignin peroxidase (LiP) enzyme in *Pichia pastoris*. In the first experiment, a gene (*lacZ*) capable of producing a beta-galactosidase, which converts a colorless X-gal substrate into an indigo-colored product (allowing visual screening), will be combined with the LiP. The *lacZ* gene (3.1kbp) was amplified by a polymerase chain reaction (PCR), using the primer pair developed by the project and the pBAD-TOPO/*LacZ* standard vector (Invitrogen) as a template. In order to fuse the *lacZ* gene with the lignin peroxidase gene, the new forward and reverse primers carry two flanking *NotI* restriction sites. This required several experiments with different *Taq* polymerases to optimize product formation. The pPICZ plasmid vectors were also isolated and restricted with *NotI*, and ligated with the *lacZ* fragment. The clones are being screened for a proper fragment insertion.

A second experiment is being conducted with the goal of reducing Guanine+Cytosine (GC) content of the LiP gene, since the *Pichia pastoris* genome has a lower GC content than the original LiP gene. Three primer fragments with lower GC content were designed for this purpose. They were used to prepare three DNA fragments extending over different regions of the gene, encompassing the complete gene. One of the primers was unsuccessful in producing the fragment. This region will be replaced by the unmodified portion of the gene. The complete gene is being reassembled with these new fragments, and will be screened for improved activity. These two experiments will be completed within the next two months, after which a final report will be issued.

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Highlights:

- Progress continues in data analyses from sampling intensives.
- Construction on inorganic aerosol sub-model begins.
- Paper describing data from Clovis house completed.
- EPA Associate Director of Health visits LBNL.

Level I analysis consists of ascertaining the precision of the various particle measurements. Level II analysis intercompares measurements to ascertain accuracy. Level II validation was completed for automated fall nitrate, fall sulfate, and fall and winter carbon measurements. Comparison to filter-based values for the intensive study periods at the Clovis house yields correlations with R2=0.97, 0.96, 0.86 for nitrate, sulfate, and carbon, respectively. While the automated nitrate and sulfate measurements concur with the filter-based measurements, the measured automated carbon values are consistently lower than the carbon filter measurements.

Diurnal patterns and concentrations for nitrate, sulfate, and black carbon were compared to those at the regional monitoring station, Fresno First St. Project researchers found that indoor/outdoor differences at the house are much larger than differences between the regional monitoring site and immediately

outside the house. This provides support for the hypothesis that it is possible to model indoor concentrations from time- and species-resolved measurements at a central monitoring site.

Progress on Model Development

Model development focused on incorporating measured data from the Clovis intensives into the model framework. Project researchers incorporated the air change data, the size-resolved particle data, the chemically resolved particle data from the automated time- and species-resolved particle instruments, and the gas phase data from the denuder/Ion Chromatograph system. Initial results from this work confirm earlier observations that the reduction in indoor relative to outdoor $PM_{2.5}$ is largely due to loss of nitrate particulate matter. Currently, project researchers are investigating different parameterizations for particle ammonium nitrate dissociation to model the nitrate PM loss that occurs as a result of crossing the building shell and entering the indoor environment. Researchers initiated efforts toward construction of an inorganic aerosol submodel to describe nitrate transformations inside residences.

Technology Transfer

A draft of a paper describing an analysis of the near real-time chemically resolved data from the intensive measurement periods for the Clovis house was completed.

Progress continues on a paper describing ammonia and nitric acid measurements and on a paper describing particle penetration and deposition.

The Environmental Protection Agency (EPA) Associate Director of Health visited LBNL for three days in September, 2001. LBNL staff held a full-day forum on the Outdoor/Indoor $PM_{2.5}$ study to inform the EPA of study results.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

Highlights:

- Data from key studies obtained for modeling and validation.
- Apparatus tested.
- EPA Associate Director of Health briefed on project.

Recent and ongoing studies that measure time-integrated volatile organic compound (VOC) concentrations both indoors and outdoors in U.S. and European residences were reviewed. Project researchers are obtaining data from key studies for analysis to guide modeling and validation efforts.

Studies of adsorption and re-emission rate constants for VOCs on typical indoor surface materials were reviewed. This data may be used and/or extrapolated for modeling of short-term sorption and re-emission kinetics of structurally similar VOCs.

Project researchers tested apparatus to investigate sorption dynamics of individual hazardous air pollutants on individual indoor surfaces in order to supplement data available from other studies.

The Environmental Protection Agency (EPA) Associate Director of Health visited LBNL for three days in September. LBNL staff briefed him on the Outdoor/Indoor VOC study to inform the EPA of the project.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization

(ORNL and ANL)

Highlights:

- Mechanism of reduction of sulfur substrates by anaerobic organisms investigated.
- Meeting planned with University of Georgia researcher.

This project investigates the potential of enzymatic and biomimetic catalysts for hydrogenation of oil compounds with the goal of upgrading crudes via sulfur removal and potential molecular weight reduction.

Project researchers investigated the mechanism of reduction of sulfur substrates by anaerobic organisms. It was found that the first step in the hydrogenation process is the hydrogenase enzyme, which splits hydrogen into a proton, an electron, and a hydride species. The electron, which is the reducing agent

and the active species, is then transferred to the sulfur substrate via a second enzyme through an electron transport chain. The proton, expelled by the hydrogenase, reacts with the sulfur substrate by being transported via the bulk phase. The key to the hydrogen splitting is the active site of the hydrogenase made up of nickel and iron as the metal centers. The active site, which harbors the electron and hydride species after the split-up, can potentially be used as the catalytic site to reduce organosulfur compounds. Project efforts are focused on improving the binding of the substrates near the active site. Relevant amino acid sites are being investigated for the type of covalent attachment with hydrophobic groups. The anaerobic setup required for microbiological work as well as that for enzyme assays, which include the gassing station and the anaerobic chamber, are in final stages of completion.

A meeting was set up with Dr. Mike Adams for January 14, 2001 to discuss sulfur assay development and purification of the thermophilic hydrogenase enzyme at the University of Georgia laboratory, in Athens. The purification of the mesophilic hydrogenase enzyme from *D. gigas* will be conducted at ORNL. Project researchers are in the process of acquiring the necessary supplies, resins, and membranes for the individual chromatography and ultrafiltration unit operations necessary for separation.

Ultra-Clean Fuels Technology

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

Highlights:

- Experimental results presented at AIChE Annual meeting.
- Revised manuscript sent for review.

Efforts in November and December focused on communication of technical results. Data on the reaction/regeneration work using both model and commercial feeds was presented at the American Institute of Chemical Engineers (AIChE) annual meeting held November 5, 2001 in Reno, NV. A revised manuscript, describing the on-line addition of inert supercritical fluids for catalyst activity extension, was sent to Industrial and Engineering Chemistry Research for review.

Experimental efforts have been put on hold until FY02 funding is received.